

The Oscillator Strengths of H_2^+ , $1s\sigma_g - 2p\sigma_u$, $1s\sigma_g - 2p\pi_u$

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The oscillator strengths of the H_2^+ molecular ion, $1s\sigma_g - 2p\sigma_u$, $1s\sigma_g - 2p\pi_u$ are calculated within the Born-Oppenheimer approximation. The variational expansion with randomly chosen exponents has been used for numerical studies. The oscillator strengths obtained for the transitions $1s\sigma_g - 2p\sigma_u$, $1s\sigma_g - 2p\pi_u$ of H_2^+ are accurate up to ten significant digits. Results are given for the internuclear distances between 0.10 and 20.0 a.u.

I. INTRODUCTION

Many theoretical calculations on the oscillator strengths of the H_2^+ molecular ion have been performed since the publication of the first [1] of Mulliken's series of papers on the subject. Bates and his co-workers had done a great deal of work on this molecular system, with special emphasis on the electronic transition probabilities for fixed internuclear separation R for a large number of electronic transitions [2–6]. The problem was formulated in terms of Jaffe's solution [7] and led to certain integrals in the expression for the transition probabilities which required numerical evaluation. Moreover, using the Hylleraas solution [8] the matrix elements of the electric dipole moment for transition between bound electronic states of the H_2^+ molecular ion for any fixed internuclear separation R have been obtained in analytical form [9]. In the last years, with the aid of the new types of variational expansions based on the randomly chosen exponents for the Coulomb three-body problem [10, 11], within the Born-Oppenheimer approximation, very accurate non-relativistic energies and the improved relativistic corrections of $m\alpha^4$ and $m\alpha^6$ orders for the ground state of the ion, as well as the more accurate static dipole polarizability for the $1s\sigma_g$ electronic state of H_2^+ molecular ion have been obtained in [12–14].

In this work our goal is to obtain more accurate values for the oscillator strengths of the $1s\sigma_g - 2p\sigma_u$, $1s\sigma_g - 2p\pi_u$ transitions of H_2^+ molecular ion within the Born-Oppenheimer approximation than those in [2] and [15].

We want to show that the use of the variational expansion suggested in this work allows an analytical evaluation of the matrix elements and can provide us with very accurate data. In future studies it can be used to obtain more accurate values of moments functions $S_k(R)$ as a function of internuclear separation R for the $1s\sigma_g$ electronic state of the H_2^+ molecular ion in the Born-Oppenheimer approximation.

II. THEORY

In what follows we consider the Coulomb two-center problem with the nonrelativistic Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + V, \quad V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}. \quad (1)$$

where r_1 and r_2 are the distances from an electron to nuclei 1 and 2, respectively.

The oscillator strength f_{0n} (details can be found in [1, 2]) can be expressed as

$$f_{0n} = \frac{2}{3} G |Q|^2 (E_n - E_0) \quad (2)$$

where G is the orbital degeneracy factor, and $G = 1$ for σ states, $G = 2$ for π states. Here Q is the transition moments and can be written in the form

$$Q = \langle 0 | r | n \rangle, \quad (3)$$

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where r is a distance of the electron from the center along the internuclear axis:

$$r = \frac{1}{2R} \sqrt{2r_1^2 r_2^2 + 2r_1^2 R^2 + 2r_2^2 R^2 - r_1^4 - r_2^4 - R^4}.$$

III. VARIATIONAL APPROXIMATION AND NUMERICAL RESULTS

In order to get a precise solution for the Schrödinger equation

$$\left[\frac{\mathbf{p}^2}{2m} + V \right] \Psi_0(\mathbf{r}) = E_0 \Psi_0(\mathbf{r}) \quad (4)$$

we use the variational approach. A variational wave function for the electronic states of the H_2^+ should be symmetrized and is constructed as follows:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{im\varphi} r^{|m|} \sum_{i=1}^{\infty} C_i (e^{-\alpha_i r_1 - \beta_i r_2} \pm e^{-\beta_i r_1 - \alpha_i r_2}), \quad (5)$$

where (+) is used for the *gerade* electronic state and (−) is for the *ungerade* electronic state, respectively. Parameters α_i and β_i are generated in quasi-random manner [10, 11]

$$\alpha_i = \left\lfloor \frac{1}{2} i(i+1) \sqrt{p_\alpha} \right\rfloor (A_2 - A_1) + A_1 \quad (6)$$

$[x]$ designates the fractional part of x , p_α is a prime number, an interval $[A_1, A_2]$ is a real variational interval, which has to be optimized. Parameters β_i are obtained in a similar way.

Numerical evaluation of the matrix elements for operators in (2) and (3) is expounded in the Appendix.

In Tables I the energy differences and oscillator strengths as a function of internuclear separation R for $1s\sigma_g - 2p\sigma_u$ transitions ($E_1 - E_0$ and f_{01}) and $1s\sigma_g - 2p\pi_u$ transitions ($E_2 - E_0$ and f_{02}) and comparisons with the previous results are presented. The estimated accuracy of obtained values for the transitions is ten significant digits. In Table II the convergence of the $1s\sigma_g - 2p\sigma_u$ and $1s\sigma_g - 2p\pi_u$ transitions with an increase in the expansion length of the Ψ (equation (5)) is demonstrated for some values of internuclear distance R .

In order to get accurate results we use three sets of basic functions of the type (5) (in a spirit of Ref.[10]) for small values of internuclear distance R , two sets for intermediate and large values of R , respectively. Total number of the basic function varies from $N = 90$ to $N = 180$. In Table II in the second and third columns the numbers of the basis functions employed (equation (5)) for the electronic states $2p\sigma_u$ and $2p\pi_u$ of H_2^+ are presented, respectively. In our calculations arithmetics of sextuple precision (about 48 decimal digits) implemented as a FORTRAN90 module has been used.

In all tables the factor x in the brackets means 10^x . Atomic units are used throughout.

IV. CONCLUSION

The oscillator strengths of the H_2^+ molecular ion, H_2^+ , $1s\sigma_g - 2p\sigma_u$, $1s\sigma_g - 2p\pi_u$ have been calculated accurately within the Born-Oppenheimer approximation. The variational expansion with randomly chosen exponents has been used for numerical studies. This type of expansion allows us to use few number of basic functions, and even the non-relativistic energy for the $1s\sigma_g$ electronic state of the ion can be obtained to 10^{-20} a.u. accuracy when the number of basis functions is less than $N = 100$ [14].

Previous calculations for the $1s\sigma_g - 2p\sigma_u$ transitions of the ion for a fairly-restricted internuclear distance R are by Mulliken [1], Bates [2], and Dalgarno and Poots [6]. Mulliken [1] used the LCAO approximation and Bates [2] employed the exact two-center wave function for the numerical integral evaluation. Dalgarno and Poots [6] employed the variational method in the calculation. The calculations for the $1s\sigma_g - 2p\pi_u$ transition of H_2^+ are by Bates, Darling, Hawe and Stewart [4], Herman and Wallis [9] and Ramaker and Peek [15]. Bates *et al* [4] used also the exact two-center wave function for the numerical integration. Herman and Wallis [9] obtained the matrix elements for the transitions between bound electronic states of the ion for any fixed internuclear distance R in an analytical form using the Hylleraas solution for the wave functions. Ramaker and Peek [15] performed the calculations for the dipole strengths of the H_2^+ molecular ion as functions of wide range of internuclear separation R for all transitions the states which correlate to a proton-plus-hydrogen-atom and have principal quantum number $n = 1, 2$ or 3 , using the exact electronic two-center wave function.

In Table III, we compare our results with earlier ones, which demonstrate the superiority of the newly obtained results. The results obtained for the transitions $1s\sigma_g - 2p\sigma_u$, $1s\sigma_g - 2p\pi_u$ of H_2^+ are accurate up to ten significant digits, that is, six digits more than in [2, 15]. With the help of the results obtained in this *Letter*, one can recalculate the mean excitation energy for the $1s\sigma_g$ electronic state of the H_2^+ molecular ion employing the functional form of the moment functions $S_k(R)$ [16–18]. This work is in progress now.

Appendix: Analytical evaluation of the matrix elements

The calculation of the matrix elements is reduced to evaluation of integrals of the type

$$\Gamma_{lm}(\alpha, \beta) = \int r_1^{l-1} r_2^{m-1} e^{-\alpha r_1 - \beta r_2} d^3 \mathbf{r}. \quad (\text{A-1})$$

Integers (l, m) are, in general, non-negative, but in case of singular matrix elements one of the indices can be negative.

The function Γ_{00} can be easily obtained

$$\Gamma_{00}(\alpha, \beta, R) = \frac{4\pi}{R} \frac{e^{-\beta R} - e^{-\alpha R}}{\alpha^2 - \beta^2}, \quad (\text{A-2})$$

where R is the distance between nuclei, then $\Gamma_{lm}(\alpha, \beta; R)$ for non-negative (l, m) may be generated from (A-2) by means of relation

$$\Gamma_{lm}(\alpha, \beta; R) = \left(-\frac{\partial}{\partial \alpha}\right)^l \left(-\frac{\partial}{\partial \beta}\right)^m \Gamma_{00}(\alpha, \beta, R). \quad (\text{A-3})$$

Integral $\Gamma_{-1,0}(\alpha, \beta; R)$ is expressed by

$$\Gamma_{-1,0}(\alpha, \beta; R) = \frac{2\pi}{R\beta} \left\{ e^{\beta R} E_1(R(\alpha + \beta)) + e^{-\beta R} \ln R(\alpha + \beta) - e^{\beta R} [E_1(R(\alpha - \beta)) + \ln R(\alpha - \beta)] \right\}. \quad (\text{A-4})$$

Worthy to note that a function in square brackets is analytic when argument is zero. Integrals $\Gamma_{-1,m}$ are generated from $\Gamma_{-1,0}$ similar to (A-3):

$$\Gamma_{-1,m}(\alpha, \beta; R) = \left(-\frac{\partial}{\partial \beta}\right)^m \Gamma_{-1,0}(\alpha, \beta, R). \quad (\text{A-5})$$

Function $E_1(z)$ encountered in (A-4) is the exponential integral function [19]:

$$E_1(z) = \Gamma(0, z) = \int_z^\infty t^{-1} e^{-t} dt.$$

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- [1] R.S. Mulliken, J. Chem. Phys. **7**, 14 (1939)
 - [2] D.R. Bates, J. Chem. Phys. **19**, 1122 (1951)
 - [3] D.R. Bates and G. Poots, Proc. Phys. Soc. A **66**, 784 (1953)
 - [4] D.R. Bates, R.T.S. Darling, S.C. Hawe and A.L. Stewart, Proc. Phys. Soc. A **66**, 1124 (1953)
 - [5] D.R. Bates, R.T.S. Darling, S.C. Hawe and A.L. Stewart, Proc. Phys. Soc. A **67**, 533 (1954)
 - [6] A. Dalgarno and G. Poots, Proc. Phys. Soc. A **67**, 343 (1954)
 - [7] G. Jaffe, Zs. f. Phys. **87**, 535 (1934)
 - [8] E.A. Hylleraas, Zs. f. Phys. **71**, 739 (1931)
 - [9] R. Herman and R.F. Wallis, Astrophys. J. **123**, 353 (1956)
 - [10] V.I. Korobov, Phys. Rev. A. **61**, 064503 (2000)
 - [11] D.H. Bailey and A.M. Frolov, J. Phys. B. **35**, 4287 (2002)
 - [12] Ts. Tsogbayar and V.I. Korobov, J. Chem. Phys. **125**, 024308 (2006)
 - [13] V.I. Korobov and Ts. Tsogbayar, J. Phys. B. **40**, 2661 (2007)
 - [14] Ts. Tsogbayar, J. Phys. B. **42**, 165007 (2009)
 - [15] D.E. Ramaker and J.M. Peek, Atom. Data. **5**, 167 (1973)
 - [16] J.D. Garcia, Phys. Rev. **147**, 66 (1966)
 - [17] J.I. Gersten, J. Chem. Phys. **51**, 3181 (1969)
 - [18] D.M. Bishop and L.M. Cheung, J. Phys. B. **11**, 3133 (1978)
 - [19] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions*. Dover Edition, New York, 1980.

TABLE I: Data on the $1s\sigma_g - 2p\sigma_u$, $1s\sigma_g - 2p\pi_u$ transitions of H_2^+

R	$E_1 - E_0$	Bates [2]		$E_2 - E_0$	Ramaker and Peek [15]	
		f_{01}	f_{01}		f_{02}	f_{02}
0.10	0.147 757 4626(1)		0.141 946 1197	0.147 857 3935(1)		0.281 958 4589
0.20	0.142 594 2876(1)	0.150	0.149 966 1487	0.142 993 1822(1)		0.292 176 8241
0.30	0.136 065 8191(1)		0.161 227 2533	0.136 960 1755(1)		0.305 026 4125
0.40	0.128 996 9831(1)	0.175	0.174 800 4051	0.130 578 7951(1)		0.318 871 6774
0.50	0.121 810 2535(1)		0.190 006 5537	0.124 264 4532(1)		0.332 827 2240
0.60	0.114 717 4343(1)	0.207	0.206 235 8257	0.118 218 5058(1)		0.346 408 7672
0.70	0.107 822 0761(1)		0.222 877 7173	0.112 529 8372(1)		0.359 356 2504
0.80	0.101 173 4174(1)	0.240	0.239 317 2609	0.107 228 2899(1)		0.371 539 1200
0.90	0.947 946 4449		0.254 970 6910	0.102 313 0356(1)		0.382 902 9462
1.00	0.886 972 6883	0.269	0.269 336 9702	0.977 678 3571	0.393	0.393 438 1322
1.30	0.721 475 3157		0.301 731 0394	0.861 082 3079		0.420 300 6176
1.50	0.625 821 6700	0.314	0.313 859 3007	0.797 263 3391	0.435	0.434 630 6848
1.80	0.503 578 1216	0.321	0.320 620 5783	0.717 917 7718	0.451	0.451 551 8442
2.00	0.435 099 8223	0.319	0.319 763 3919	0.673 862 3946	0.460	0.460 186 9855
2.30	0.349 292 2274		0.313 481 1372	0.618 286 6408		0.469 722 4456
2.50	0.301 751 4622	0.307	0.307 111 6776	0.587 007 7894	0.474	0.474 048 0566
2.80	0.242 384 3555	0.297	0.295 449 1732	0.547 111 4888	0.478	0.477 811 5429
3.00	0.209 477 8640	0.289	0.286 648 3110	0.524 452 3451	0.479	0.478 648 2112
3.50	0.145 359 8123	0.264	0.262 040 2032	0.478 772 9801	0.475	0.475 449 5457
4.00	0.100 534 2444	0.238	0.234 600 2369	0.445 260 2396	0.465	0.465 523 7278
4.50	0.691 110 5645(-1)	0.295	0.205 243 3086	0.420 759 4992	0.450	0.449 971 8773
5.00	0.471 286 8194(-1)	0.175	0.175 094 9934	0.403 035 4828	0.430	0.430 144 3360
5.50	0.318 483 6379(-1)	0.144	0.145 512 8632	0.390 423 8948	0.408	0.407 637 0403
6.00	0.213 251 5610(-1)	0.116	0.117 844 6702	0.381 644 1528	0.384	0.384 106 9351
6.50	0.141 551 5325(-1)	0.090	0.931 480 9973(-1)	0.375 699 5692	0.361	0.361 026 7789
7.00	0.932 229 1695(-2)	0.069	0.720 267 2925(-1)	0.371 819 5628	0.339	0.339 507 0520
7.50	0.609 732 1052(-2)	0.090	0.546 252 3165(-1)	0.369 418 4230	0.320	0.320 242 4604
8.00	0.396 437 2998(-2)	0.039	0.407 352 9645(-1)	0.368 059 7573	0.304	0.303 561 4626
8.50	0.256 445 4385(-2)	0.028	0.299 374 4120(-1)	0.367 424 2386	0.289	0.289 523 5398
9.00	0.165 162 3429(-2)	0.020	0.217 256 4226(-1)	0.367 281 4212	0.278	0.278 018 0087
9.50	0.105 969 2322(-2)	0.016	0.155 938 7742(-1)	0.367 466 5422	0.269	0.268 841 6239
10.00	0.677 660 3412(-3)	0.011	0.110 852 7572(-1)	0.367 862 4388	0.262	0.261 750 5281
11.00	0.274 807 5098(-3)		0.546 544 7478(-2)	0.368 978 5760		0.252 815 1953
12.00	0.110 412 3031(-3)		0.262 186 7652(-2)	0.370 217 2763		0.249 293 6287
13.00	0.440 274 9253(-4)		0.122 982 9099(-2)	0.371 377 5187		0.249 503 7766
14.00	0.174 459 4699(-4)		0.566 128 7073(-3)	0.372 370 6777		0.252 027 6563
15.00	0.687 612 7753(-5)		0.256 469 7079(-3)	0.373 170 2448		0.255 725 8261
16.00	0.269 771 2233(-5)		0.114 593 6419(-3)	0.373 783 9614		0.259 757 3081
17.00	0.105 416 2788(-5)		0.505 885 9722(-4)	0.374 236 6462		0.263 577 2171
18.00	0.410 477 9229(-6)		0.220 971 2567(-4)	0.374 559 1664		0.266 896 4478
19.00	0.159 336 3912(-6)		0.956 149 8035(-5)	0.374 781 7742		0.269 614 3011
20.00	0.616 776 4338(-7)		0.410 256 5319(-5)	0.374 930 7098		0.271 746 9205

TABLE II: Convergence of the $1s\sigma_g - 2p\sigma_u$ and $1s\sigma_g - 2p\pi_u$ transitions with an increase in the basic-set size of Ψ

$R(a.u.)$	N		f_{01}	f_{02}
0.10	110	65	0.141 946 119 692 60	0.281 958 458 927 66
	125	80	0.141 946 119 692 60	0.281 958 458 927 67
	140	95	0.141 946 119 692 60	0.281 958 458 927 67
2.00	90	68	0.319 763 391 895 63	0.460 186 985 489 56
	120	78	0.319 763 391 895 63	0.460 186 985 489 56
	140	98	0.319 763 391 895 63	0.460 186 985 489 56
20.0	90	105	0.410 256 531 872 29(-5)	0.271 746 920 513 63
	110	125	0.410 256 531 861 97(-5)	0.271 746 920 515 47
	130	160	0.410 256 531 861 96(-5)	0.271 746 920 515 47

TABLE III: Comparison with earlier calculations at a bond length $R = 2.0 a.u.$

	f_{01}	f_{02}
Mulliken [1]	0.31	
Dalgarno and Poots [6]	0.319	
Bates <i>et al</i> [2, 4]	0.319	0.460
Ramaker and Peek [15]	0.319	0.460
This work	0.319 763 3919	0.460 186 9855